



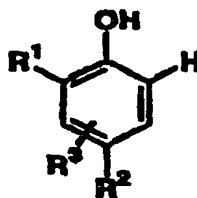
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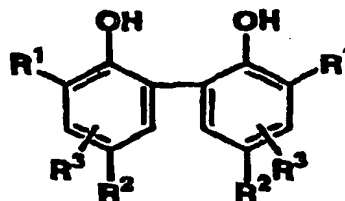
(54) Title: METHOD FOR PRODUCING 2,2'-DIHYDROXYBIPHENYLS

(57) Abstract

A method is provided for producing 2,2'-dihydroxybiphenyls represented by formula (II), wherein R¹ represents a hydrogen atom, an alkyl group, a cycloalkyl group, an alkylcycloalkyl group, an aralkyl group or a phenyl group, R² represents an alkyl group, a cycloalkyl group, an alkylcycloalkyl group, an aralkyl group or a phenyl group, and R³ represents a hydrogen atom or an alkyl group, which method comprises: reacting a phenol compound represented by formula (I), wherein R¹, R² and R³ are as defined above, with (i) hydrogen peroxide in water in the presence of a carboxylic acid or a salt thereof and a base, or (ii) oxygen in a dichlorobenzene in the presence of cuprous halide and ethylenediamine or an ethylenediamine in which at least one of the amino groups is substituted with an alkyl group.



(I)



(II)

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METHOD FOR PRODUCING 2,2'-DIHYDROXYBIPHENYLS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method for producing 2,2'-dihydroxybiphenyls. More particularly, the present invention relates to a method for producing 2,2'-dihydroxybiphenyls which comprises reacting corresponding phenol compounds with (i) hydrogen peroxide in water in the presence of a carboxylic acid or a salt thereof and a base; or (ii) oxygen in dichlorobenzene in the presence of cuprous halide and ethylenediamine or an ethylenediamine in which at least one of amino groups thereof is substituted with an alkyl group.

Description of the Related Art

2,2'-Dihydroxybiphenyls have been used as a ligand of an optically active metal complex catalyst, an intermediate of a stabilizer for organic materials, or the like.

It is known that 2,2'-dihydroxybiphenyls can be produced by reacting corresponding phenol compounds with hydrogen peroxide. It is proposed that the reaction is conducted, for example, in water in the presence of sodium laurylsulfate and a base (JP-A-56-135432).

However, when the resulting reaction mass is neutralized with an acid, then is extracted with an organic

solvent for providing 2,2'-dihydroxybiphenyl in the form of an organic solvent solution, which is the favorable form for its transportation, the mass becomes emulsified and a liquid separation required to obtain the solution cannot be conducted. Therefore, it was difficult to obtain the intended organic solvent solution of 2,2'-dihydroxybiphenyls by an extraction of the reaction mass with an organic solvent.

It is also known that 2,2'-dihydroxybiphenyls can be produced by reacting corresponding phenol compounds with oxygen. For example, a method for the reaction has been proposed in which the reaction is conducted in methanol in the presence of cupric chloride and ethylenediamine or an ethylenediamine in which at least one of amino groups is substituted with an alkyl group, such as ethylenediamine, tetramethylethylenediamine, tetraethylethylenediamine and the like (J. Org. Chem. Vol. 49, 4456 (1984)). Another method for the reaction is also proposed in which the reaction is conducted in acetonitrile in the presence of cuprous chloride (Tetrahedron Letters, Vol. 24, No. 50, 5611 (1983)).

However, according to these methods, the yield of intended 2,2'-dihydroxybiphenyls is as low as 30 to 60%, and thus an improvement in yield has been desired.

Another method has also been proposed in which reaction is conducted in ethanol in the presence of cuprous chloride and tetramethylethylenediamine to form an intermediate spiroquinol compound, which is then isolated and reacted with the phenol compounds without solvent or in acetic

acid(US-Patent No. 3,549,712).

However, since this method is a two-step reaction in which an intermediate is made, isolated from the reaction mass and reacted again, the operation thereof is complicated and an apparatus for isolating the intermediate is required. Further, the obtained yield thereof is not sufficient and an improvement in yield has been desired.

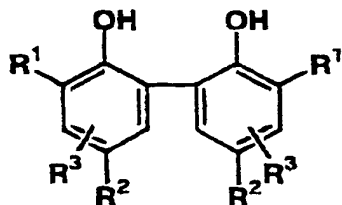
SUMMARY OF THE INVENTION

The present inventors have intensively studied for a method for providing an organic solvent solution of 2,2'-dihydroxybiphenyls, and, as a result, have found that 2,2'-dihydroxybiphenyls can be easily extracted from the reaction mass into an organic solvent if a carboxylic acid or a salt thereof is used instead of sodium laurylsulfate in the reaction of a corresponding phenol compound with hydrogen peroxide, and that an organic solution thereof can be easily obtained.

Further, the present inventors have intensively studied for a reaction of phenol compounds with oxygen to find an excellent method for producing 2,2'-dihydroxybiphenyls, and, as a result, found that an intended compound can be obtained efficiently and in one-step reaction carried out in dichlorobenzene in the presence of cuprous halide and ethylenediamine or an ethylenediamine in which at least one of the amino groups is substituted with an alkyl group. The present invention has thus been completed.

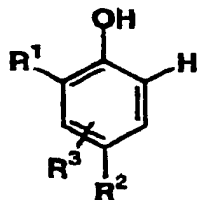
More particularly, in a first embodiment thereof, the

present invention provides a method for producing industrially excellent 2,2'-dihydroxybiphenyls represented by the formula (II):



(II)

wherein R¹ represents a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group, which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, R² represents an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, and R³ represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, which comprises reacting a phenol compound represented by the formula (I):



(I)

wherein R¹, R² and R³ are as defined above, with hydrogen peroxide in water in the presence of a carboxylic acid or a salt thereof and a base.

Similarly, in a second embodiment thereof, the present invention also provides a method for producing industrially excellent 2,2'-dihydroxybiphenyls represented by the formula (II) which comprises reacting a phenol compound represented by the formula (I) with oxygen in a dichlorobenzene in the presence of cuprous halide and ethylenediamine or an ethylenediamine in which at least one of the amino groups is substituted with an alkyl group.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in detail below.

In the present invention, R^1 in the formula (I) represents a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, R^2 represents an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, and R^3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms.

Examples of suitable alkyl groups having 1 to 8 carbon atoms include methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, t-pentyl, i-octyl, t-octyl and 2-ethylhexyl.

Examples of suitable cycloalkyl groups having 5 to 8 carbon atoms include cyclopentyl, cyclohexyl and cycloheptylcyclooctyl.

Examples of suitable alkylcycloalkyl groups having 6 to 12 carbon atoms include 1-methylcyclopentyl, 1-methylcyclohexyl and 1-methyl-4-i-propylcyclohexyl

Examples of suitable aralkyl groups having 7 to 12 carbon atoms include benzyl, phenylethyl, α -methylbenzyl and α, α -dimethylbenzyl.

As the phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, unsubstituted phenyl and phenyls substituted with the above-exemplified alkyl groups having 1 to 8 carbon atoms are exemplified. Specific examples thereof include methylphenyl, ethylphenyl, n-propylphenyl, i-propylphenyl, n-butylphenyl, i-butylphenyl, sec-butylphenyl, t-butylphenyl, t-pentylphenyl, i-octylphenyl, t-octylphenyl and 2-ethylhexylphenyl.

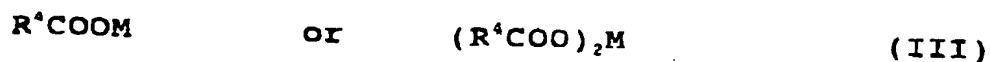
R^1 and R^2 , which may be same to or different from each other, are preferably an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms or an alkylcycloalkyl group having 6 to 12 carbon atoms, more preferably an alkyl group having 1 to 8 carbon atoms.

More preferably, R^1 is a t-alkyl such as t-butyl, t-pentyl and t-octyl. More preferably, R^2 is methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, t-butyl, t-pentyl and the like, particularly preferably methyl, t-butyl, t-pentyl and the like. Preferably R^3 is a hydrogen

atom or an alkyl having 1 to 5 carbon atoms, particularly preferably a hydrogen atom or a methyl group and the like.

Examples of the phenol compounds of formula (I) include p-cresol, p-ethylphenyl, p-propylphenol, p-isopropylphenol, p-n-butylphenol, p-sec-butylphenol, p-t-butylphenol, p-t-amylphenol, p-t-octylphenol, p-nonylphenol, p-phenylphenol, 2,4-dimethylphenol, 2,4-diethylphenol, 2-t-butyl-4-methylphenol, 4-t-butyl-2-methylphenol, 2-t-butyl-4-ethylphenol, 2-t-butyl-4-isopropylphenol, 2,4-di-t-butylphenol, 2,4-di-t-amylphenol, 2,4-di-t-octylphenol, 2-(1-methylcyclohexyl)-4-methylphenol, 2-cyclohexyl-4-methylphenol, 4-t-butyl-2-phenylphenol, 2,4,5-trimethylphenol, 2-t-butyl-3-ethyl-4-methylphenol and 2,4-di-t-butyl-5-methylphenol. Among them, 2,4-di-t-butylphenol, 2,4-di-t-amylphenol, 2,4-di-t-octylphenol and the like are preferred.

The carboxylic acid or salt thereof that is present during the reaction of the phenol compound of formula (I) with hydrogen peroxide may be represented, for example, by the following formula (III):



wherein R^4 represents an alkyl group having 6 to 17 carbon atoms, an alkenyl group having 6 to 17 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group, and M represents a hydrogen atom, an alkali metal or an alkali

earth metal.

Examples of the alkyl group having 6 to 17 carbon atoms represented by R' in the formula (III) include n-hexyl, n-heptyl, n-octyl, t-octyl, n-nonyl, n-decyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl and n-heptadecyl. Examples of the alkenyl group having 6 to 17 carbon atoms represented by R' in the formula (III) include heptadecenyl. Furthermore, as the cycloalkyl group having 5 to 8 carbon atoms, alkylcycloalkyl groups having 6 to 12 carbon atoms and aralkyl group having 7 to 12 carbon atoms represented by R' in the formula (III), the same cycloalkyl groups, alkylcycloalkyl groups and aralkyl groups as listed above are exemplified.

Examples of the alkali metal represented by M in formula (III) include sodium, potassium, lithium and cesium. Examples of the alkali earth metal represented by M in formula (III) include calcium, magnesium and barium.

Examples of the carboxylic acid and salt thereof present during the reaction of the phenol compound of formula (I) with hydrogen peroxide include sodium n-decanoate, potassium n-decanoate, n-decanoic acid, sodium laurate, potassium laurate, lauric acid, sodium myristate, potassium myristate, myristic acid, sodium palmitate, potassium palmitate, palmitic acid, sodium stearate, potassium stearate, stearic acid, sodium oleate, potassium oleate and oleic acid. Among them, sodium laurate, lauric acid and the like are preferred.

The carboxylic acid and salt thereof are used usually

in an amount of from about 0.1 to 10 mol% based on the amount of the phenol compound of formula (I).

Examples of the base that is present during the reaction of the phenol compound of formula (I) with hydrogen peroxide include hydroxides and carbonates of alkali metals such as sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate and cesium carbonate; and hydroxides and carbonates of alkali earth metals such as calcium hydroxide, barium hydroxide, magnesium hydroxide, calcium carbonate, barium carbonate and magnesium carbonate.

The base, when used, is usually present in an amount of from about 0.5 to 4 mol based on the amount of the phenol compound of formula (I).

Hydrogen peroxide, when reacted with the phenol compound of formula (I), is usually used in the form of an aqueous solution of about 0.5 to 65% by weight. The amount thereof used is usually from about 0.3 to 2 mol based on 1 mol of the phenol compound of formula (I).

Water, as the solvent, is usually used in an amount of from about 0.5 to 10 times by weight based on the amount of the phenol compound of formula (I).

The reaction of the phenol compound of formula (I) with hydrogen peroxide is usually carried out by adding hydrogen peroxide to a mixture containing water, carboxylic acid or a salt thereof, the base and the phenol compound of formula (I). The reaction temperature is usually from about 20 to 90°C, and the progress of the reaction can be traced by liquid

chromatography.

Thus, the intended 2,2'-dihydroxybiphenyls of formula (II) are produced by reacting a phenol compound of formula (I) with hydrogen peroxide in water in the presence of a carboxylic acid or a salt thereof and a base.

Extraction of the intended material, 2,2'-dihydroxybiphenyls of formula (II), from the reaction mass with an organic solvent is usually carried out in the following manner: an organic solvent is added to the reaction mass which is neutralized with an acid, then the extraction is carried out and the organic layer is separated. Before adding the organic solvent, the reaction mass is usually treated with a reducing agent such as sodium sulfite and the like.

Preferred examples of the acid used for the extraction include mineral acids such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid and the like.

Examples of the organic solvent used for the extraction include aromatic hydrocarbon solvents such as benzene, toluene, xylene and ethylbenzene, aliphatic hydrocarbon solvents such as n-hexane, n-heptane and cyclohexane, ether solvents such as diethyl ether, dibutyl ether, diisopropyl ether and tetrahydrofuran, ester solvents such as ethyl acetate, ketone solvents such as diisobutyl ketone, diisopropyl ketone and methylisobutyl ketone, halogenated aliphatic hydrocarbon solvents such as dichloromethane and chloroform, halogenated aromatic hydrocarbon solvents such as monochlorobenzene and dichlorobenzene. The organic

solvent is usually used in an amount of from about 0.5 to 10 times by weight based on the amount of the phenol compound of formula (I).

The resulting organic solvent solution obtained in the extraction described above can be washed with water to reduce the content of inorganic components and the like, and can also be subjected to a purification treatment such as activated carbon treatment and the like to be further purified. Thus, the intended organic solvent solution of 2,2'-dihydroxybiphenyls of formula (II) is produced.

Accordingly, in the present invention, 2,2'-dihydroxybiphenyls of formula (II) can be efficiently obtained by reacting a phenol compound of formula (I) with hydrogen peroxide in water in the presence of a carboxylic acid or a salt thereof and a base, and can be easily extracted from the reaction mass into an organic solvent, with the intended organic solvent solution easily being obtained in high yield.

As described above, the present invention also provides a method for producing industrially excellent 2,2'-dihydroxybiphenyls of formula (II) which comprises reacting a phenol compound represented by the formula (I) with oxygen in a dichlorobenzene solvent in the presence of cuprous halide and ethylenediamine or an ethylenediamine in which at least one of the amino groups thereof is substituted with an alkyl group.

Examples of the dichlorobenzene solvent include o-dichlorobenzene, m-dichlorobenzene and mixtures thereof.

Among them, o-dichlorobenzene is preferably used.

This dichlorobenzene is used usually in an amount of about 0.5 to 20 times by weight based on the amount of the phenol compound of formula (I).

Examples of the cuprous halide include cuprous chloride, cuprous bromide and cuprous iodide. Usually, cuprous chloride and cuprous bromide, particularly cuprous chloride, are used. The cuprous halide is used usually in an amount of about 0.01 to 10 mol% based on the amount of the phenol compounds of formula (I).

Examples of the alkyl group as a substituent on the amino group in the substituted ethylenediamine include an alkyl group having 1 to 8 carbon atoms same as described above. Among ethylenediamine and the ethylenediamine in which at least one of the amino groups thereof is substituted with an alkyl group, preferable are ethylenediamine, and ethylenediamine in which at least one of the amino groups thereof is substituted with an alkyl group having 1 to 4 carbon atoms. The amount thereof used is preferably from 0.01 to 10 mol% based on the amount of the phenol compound of formula (I).

Typical examples of the ethylenediamine in which at least one amino groups thereof is substituted with an alkyl group include N-methylethylenediamine, N-ethylethylenediamine, N,N-dimethylethylenediamine, N,N'-dimethylethylenediamine, N,N-diethylethylenediamine, N,N'-diethylethylenediamine, N,N,N'-triethylethylenediamine, N,N,N'-triethylethylenediamine,

N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetraethylethylenediamine and the like.

The oxygen reacted with the phenol compound of formula (I) may be, for example, an oxygen gas, air, or an oxygen-containing gas diluted with an inactive gas such as nitrogen gas. Usually, however, air is found suitable and utilized. The amount of oxygen should be an amount necessary and sufficient for the conversion of the phenol compound of formula (I) into 2,2'-dihydroxybiphenyls of formula (II). Usually, it is preferable that the oxygen is introduced into the reaction mixture constantly during the reaction process.

The reaction temperature is not particularly restricted but usually in the range from about 20 to 100°C.

Thus, the intended 2,2'-dihydroxybiphenyl of formula (II) is produced, and an organic solvent solution of the 2,2'-dihydroxybiphenyl of formula (II), from which a copper catalyst and the ethylenediamine have been removed, can be easily obtained in high yield. For example, it can be obtained by adding an acid such as sulfuric acid, hydrochloric acid, acetic acid and the like to the resulting reaction mass and conducting washing with water and liquid separation, or treating the resulting reaction mass with activated carbon, silica or alumina. The intended material can be obtained from the reaction mass by a separation means such as solvent distilling off and filtration, and can be further purified by a purification means such as crystallization, distillation and liquid chromatography.

Accordingly, in the present invention, the intended

2,2'-dihydroxybiphenyl compounds of formula (II) can be obtained efficiently in one-step reaction by reacting a phenol compound represented by the formula (I) with oxygen in a dichlorobenzene in the presence of cuprous halide and ethylenediamine or an ethylenediamine in which at least one of the amino groups thereof is substituted with an alkyl group.

EXAMPLES

The following examples further illustrate the present invention in detail below but do not limit the scope thereof.

Example 1

Under a nitrogen gas flow, 28.6 g of sodium hydroxide, 1.5 g of lauric acid and 233.3 g of water were charged into a flask, and the mixture was heated to 85°C with stirring. To this solution was added 147.5 g of 2,4-di-t-butylphenol, then, 41.7 g of 35% hydrogen peroxide was added dropwise, and the temperature was maintained for 3 hours to obtain a slurry. Then, to the slurry was added 18.0 g of a 10% sodium sulfite aqueous solution and 348.6 g of xylene, then, 35.8 g of 98% sulfuric acid was added for neutralization. After carrying out an extraction, the aqueous layer was separated, then, the organic layer was washed with 73.8 g of water to obtain 519.0 g of a xylene solution of 2,2'-dihydroxy-3,3',5,5'-tetra-t-butylbiphenyl.

The concentration of 2,2'-dihydroxy-3,3',5,5'-tetra-t-butylbiphenyl in this solution was measured by liquid

chromatography, and the yield was calculated and found to be 93.2%.

Examples 2 to 9

The same procedures as in Example 1 were carried out except that compounds shown in Table 1 were used instead of the lauric acid that was used in Example 1. The yields of 2,2'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl are shown in Table 1.

Table 1

Example	Compound	Yield
2	sodium n-decanoate	93.4%
3	sodium laurate	94.7%
4	potassium laurate	88.4%
5	sodium myristate	86.7%
6	sodium palmitate	82.8%
7	potassium palmitate	83.4%
8	sodium oleate	90.9%
9	potassium oleate	85.2%

Comparative Example 1

The same procedure as in Example 1 was carried out except that sodium laurylsulfate was used instead of the lauric acid that was used in Example 1. The solution after addition of xylene and sulfuric acid was emulsified, and could not be separated even after being left for 3 hours after termination of stirring.

Comparative Example 2

The same procedure as in Example 1 was carried out except that lauric acid was not used. The yield of 2,2'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl was 61.8%.

Example 10

51.6 g of 2,4-di-*t*-butylphenol, 200 g of *o*-dichlorobenzene, 124 mg of cuprous chloride and 291 mg of N,N,N',N'-tetramethylethylenediamine were charged into a flask, and the mixture was heated to 40°C with stirring. This temperature was maintained for 2 hours while introducing air continuously into the reaction solution. Thereafter, the concentration of 2,2'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl in the solution was measured by liquid chromatography, and the yield of the intended material was calculated and found to be 91.3%.

Examples 11

The same procedure as in Example 10 was carried out except that 431 mg of N,N,N',N'-tetraethylethylenediamine was used instead of N,N,N',N'-tetramethylethylenediamine and the mixture was kept at 40°C for 4 hours. The yield of 2,2'-dihydroxy-3,3',5,5'-tetra-*t*-butylbiphenyl was 88.1%.

Comparative Examples 3

The same procedure as in Example 10 was carried out except that N,N,N',N'-tetramethylethylenediamine was not

used. The intended 2,2'-dihydroxy-3,3',5,5'-tetra-t-butylbiphenyl product was scarcely produced, and the raw material, 2,4-di-t-butylphenol, was recovered.

Comparative Example 4

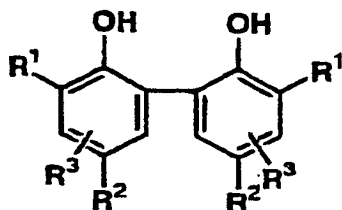
50.0 g of 2,4-di-t-butylphenol, 250 ml of ethanol, 2.00 g of cuprous chloride and 3.0 ml of N,N,N',N'-tetramethylethylenediamine were charged into a flask. Then, air was introduced continuously into the reaction vessel while stirring and heating the mixture from 25°C up to 32°C over 1 hour. Further, the mixture was heated up to 45°C while introducing air, then this temperature was maintained for 5.5 hours. The yield of 2,2'-dihydroxy-3,3',5,5'-tetra-t-butylbiphenyl was 2.4%, and the yield of the main product, 3,3',5,5'-tetra-t-butyl-spiro(3,5-cyclohexadiene-1,8'[7]oxabicyclo[4.2.0]octa[1,3,5]triene)-2-one was 64.1%.

Comparative Example 5

50.0 g of 2,4-di-t-butylphenol, 100.0 g of methanol, 202 mg of cuprous chloride and 262 mg of N,N,N',N'-tetramethylethylenediamine were charged into a flask. Then, air was introduced continuously into the reaction vessel while stirring and keeping the mixture at 25°C for 23 hours. Further, the mixture was heated up to 50°C while introducing air, and this temperature was maintained for 7 hours. The yield of 2,2'-dihydroxy-3,3',5,5'-tetra-t-butylbiphenyl was 33.6%.

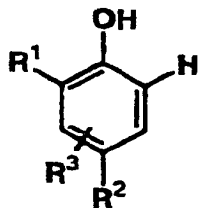
CLAIMS

1. A method for producing a 2,2'-dihydroxybiphenyl compound represented by the formula (II):



(II)

wherein R¹ represents a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group, which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, R² represents an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, and R³ represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, which method comprises reacting a phenol compound represented by the following formula (I):



(I)

wherein R¹, R² and R³ are as defined above, with hydrogen peroxide in water in the presence of a

carboxylic acid or a salt thereof and a base.

2. The method according to claim 1, wherein said phenol compound of formula (I) is present in an amount, such that the carboxylic acid or the salt thereof are present in an amount of from about 0.1 to 10 mol% based on the amount of the phenol compound of formula (I) and the base is present in an amount of from about 0.5 to 4 mol based on the amount of the phenol compound of formula (I).

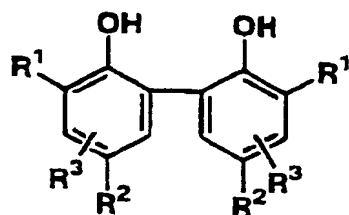
3. The method according to claim 1, wherein the carboxylic acid or the salt thereof is represented by the following formula (III):



wherein R' represents an alkyl group having 6 to 17 carbon atoms, an alkenyl group having 6 to 17 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group, and M represents a hydrogen atom, alkali metal or alkali earth metal.

4. The method according to claim 1, wherein the base is a hydroxide or a carbonate of an alkali metal, or a hydroxide or a carbonate of an alkali earth metal.

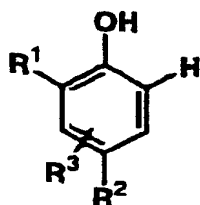
5. A method for producing an organic solvent solution of a 2,2'-dihydroxybiphenyl represented by the following formula (II):



(II)

wherein R^1 represents a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, R^2 represents an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, and R^3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, which method comprises:

reacting in a mixture a phenol compound represented by the following formula (I):



(I)

wherein R^1 , R^2 and R^3 are as defined above, with hydrogen peroxide in water in the presence of a carboxylic acid or a salt thereof and a base; adding an organic solvent to the reaction mixture; neutralizing the reaction mixture with an acid; and extracting the 2,2'-

dihydroxybiphenyl of formula (II) from the reaction mixture.

6. The method according to claim 5, wherein said phenol compound of formula (II) is present in an amount, such that the amount of the carboxylic acid or the salt thereof is from about 0.1 to 10 mol% based on the amount of the phenol compound of formula (I) and the amount of the base is from about 0.5 to 4 mol based on the amount of the phenol compound of formula (I).

7. The method according to claim 5, wherein the carboxylic acid or the salt thereof is represented by the formula (III):



wherein R^1 represents an alkyl group having 6 to 17 carbon atoms, an alkenyl group having 6 to 17 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group, and M represents a hydrogen atom, alkali metal or alkali earth metal.

8. The method according to claim 5, wherein the base is a hydroxide or a carbonate of an alkali metal, or a hydroxide or a carbonate of an alkali earth metal.

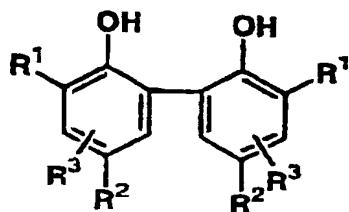
9. The method according to claim 5, wherein the acid is a mineral acid.

10. The method according to claim 5, wherein the organic solvent is selected from the group consisting of an aromatic hydrocarbon, an aliphatic hydrocarbon, an ether, an ester, a ketone, a halogenated aliphatic hydrocarbon, and a

halogenated aromatic hydrocarbon.

11. The method according to claim 5, wherein said phenol compound is present in an amount, such that the organic solvent is present in an amount of from about 0.5 to 10 times by weight based on the amount of the phenol compound of formula (I).

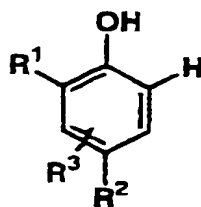
12. A method for producing a 2,2'-dihydroxybiphenyl represented by the following formula (II):



(II)

wherein R^1 represents a hydrogen atom, an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, R^2 represents an alkyl group having 1 to 8 carbon atoms, a cycloalkyl group having 5 to 8 carbon atoms, an alkylcycloalkyl group having 6 to 12 carbon atoms, an aralkyl group having 7 to 12 carbon atoms or a phenyl group which may be optionally substituted with an alkyl group having 1 to 8 carbon atoms, and R^3 represents a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, which method comprises:

reacting a phenol compound represented by the following formula (I):



(I)

with oxygen in a dichlorobenzene in the presence of a cuprous halide and ethylenediamine or an ethylenediamine in which at least one of the amino groups thereof is substituted with an alkyl group.

13. The method according to claim 12, wherein R^1 and R^2 , which may be same to or different from each other, are an alkyl group having 1 to 8 carbon atoms.

14. The method according to claim 12, wherein said phenol compound of formula (I) is present in an amount, such that the ethylenediamine or the ethylenediamine in which at least one of the amino groups thereof is substituted with an alkyl group is present in an amount of from about 0.01 to 10 mol% based on the amount of the phenol compound of formula (I).

15. The method according to claim 12, wherein the ethylenediamine in which at least one of the amino groups thereof is substituted with an alkyl group is an ethylenediamine having at least one amino group thereof substituted with an alkyl group having 1 to 4 carbon atoms.

16. The method according to claim 12, wherein said phenol compound of formula (I) is present in an amount, such that the cuprous halide is present in an amount of from about 0.01 to 10 mol% based on the amount of the phenol compound of formula (I).

17. The method according to claim 12, wherein the cuprous

halide is cuprous chloride.

18. The method according to claim 12, wherein said phenol compound of formula (I) is present in an amount, such that the dichlorobenzene is present in an amount of from about 0.5 to 20 times by weight based on the amount of the phenol compound of formula (I).

19. The method according to claim 12, wherein the reaction occurs at a temperature that is in the range of from about 20 to 100°C.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 99/01106

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C39/15 C07C37/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 035 965 A (CIBA-GEIGY AG) 16 September 1981 (1981-09-16) claims & JP 56 135432 A cited in the application	1
A	US 4 085 124 A (RUTLEDGE THOMAS F.) 18 April 1978 (1978-04-18) claims	12
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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 August 1999

Date of mailing of the international search report

25/08/1999

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Van Geyt, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 99/01106

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>K. KUSHIOKA: "Autoxidation of Phenols Catalyzed by Copper(II)-Ethylenediamine Complexes: The Reaction Mechanism" JOURNAL OF ORGANIC CHEMISTRY, vol. 49, no. 23, 1984, pages 4456-4459, — XP002111412 EASTON, US ISSN: 0022-3263 cited in the application * Abstract; Experimental Section *</p>	12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 99/01106

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